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Climate of the Past Discussions

Application of Fourier Transform Infrared Spectroscopy (FTIR) for assessing biogenic silica sample purity in geochemical analyses and palaeoenvironmental research

G. E. A. Swann[1] and S. V. Patwardhan[2]

[1]NERC Isotope Geosciences Laboratory, British Geological Survey, Keyworth, Nottingham, NG12 5GG, UK
[2]Department of Chemical and Process Engineering, University of Strathclyde, James Weir Building, 75 Montrose Street, Glasgow, G1 1XJ, UK

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Correspondence to: G. E. A. Swann (gean@bgs.ac.uk)

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Abstract

The development of a rapid and non-destructive method to assess levels of purity in samples of biogenic silica prior to geochemical/isotope analysis remains a key objective in improving both the quality and use of such data in environmental and palaeoclimatic research. Here a Fourier Transform Infrared Spectroscopy (FTIR) mass-balance method is demonstrated for calculating levels of contamination in cleaned sediment core diatom samples from Lake Baikal Russia. Following the selection of end-members representative of diatoms and contaminants in the analysed samples, a mass-balance model is generated to simulate the expected FTIR spectra for a given level of contamination. By fitting the sample FTIR spectra to the modelled FTIR spectra and calculating the Euclidean distance, the optimum best-fit model and level of contamination is obtained. When compared to X-ray Fluorescence (XRF), FTIR method results portray the main changes in sample contamination through the core sequence, permitting its use in instances where other, destructive, techniques are not appropriate. The ability to analyses samples of < 1 mg enables, for the first time, routine analyses of small sized samples. Discrepancies between FTIR and XRF measurements can be attributed to FTIR end-members not fully representing all contaminants and problems in using XRF to detect organic matter external to the diatom frustule. By analysing samples with both FTIR and XRF, these limitations can be eliminated to accurately identify contaminated samples and improve the accuracy of climate reconstructions. Future, routine, use of these techniques in palaeoenvironmental research will significantly reduce the number of erroneous measurements and so improve the accuracy of biogenic silica/diatom based reconstructions.

1 Introduction

Increased attention is focused on the potential for geochemical measurements of biogenic silica to be used in palaeoenvironmental research in both continental, riverine,

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lacustrine and marine settings (e.g., Filippelli et al., 2000; de la Rocha et al., 2000; de la Rocha, 2003, 2006; Derry et al., 2005; Hendry and Rickaby, 2008; Hodson et al., 2008; Opfergelt et al., 2008; Swann et al., 2010). These studies, most commonly involving the analysis of diatoms, plant phytoliths, radiolaria and siliceous sponges, are believed to be particularly important in attempts to better understand the global silicon cycle as well as high latitude environmental change in regions where carbonates are not readily preserved in the sediment record (Conley, 2002; Street-Perrott and Barker, 2008; Leng et al., 2009; Swann and Leng, 2009).

In spite of its potential, the generation of accurate quantitative reconstructions from sources of biogenic silica are often hindered by issues of sample contamination. Sample preparation for foraminifera, ostracods and other biogenic carbonate organisms for geochemical analyses are typically marked by the hand-picking of individual organisms, thereby largely negating issues of contamination. In contrast the smaller size of biogenic silica samples, and the larger number of organisms consequently needed for a single analysis, typically prevents similar picking. Instead, current methods for purifying/extracting biogenic silica samples involve a mixture of chemical and physical treatment stages including the use of heavy liquids and gravitational split-flow thin fractionation (SPLITT) (e.g., Giddings, 1985; Juillet-Leclerc, 1986; Shemesh et al., 1995; Ellwood and Hunter, 1999; Morley et al., 2004; Rings et al., 2004; Robinson et al., 2004; Hamilton et al., 2005; Tyler et al., 2007; Minoletti et al., 2009). Whilst these techniques can results in the extraction of fully cleaned samples, in most instances a small to moderate level of non-removable contaminants will remain. This is particularly apparent in samples where contaminants become electro-statically bound to biogenic silica (Brewer et al., 2008).

Historically the issue of sample contamination in biogenic silica geochemistry measurements has not been widely considered. Whilst spot counts performed under a light or Scanning Electron Microscope (SEM) are increasingly being employed (Morley et al., 2004), the accuracy of these checks have been questioned due to their dependency on the amount of material screened and the difficulty in accurately converting

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observations into usable estimates of biogenic silica biovolume/contaminant content (Brewer et al., 2008). Recent research has shifted towards employing trace element geochemistry as a measure of contamination using X-ray Fluorescence (XRF) in which the ionisation of a sample leads to the production of X-rays that are characteristic of the analysed sample (Brewer et al., 2008). Whilst permitting direct measures of contamination by comparing measured oxide concentrations such as Al_2O_3 and CaO to published diatom concentrations (e.g., Mackay et al., 2010a) the relatively large, 0.1–1.0 g, amounts of material required for a single analysis is often prohibitive for the technique to be used in routine analyses. One solution is the use of SEM plus Energy Dispersive X-ray Spectroscopy (EDS). However as with XRF, EDS analyses can be severely limited in quantifying certain low energy X-rays such as nitrogen and other trace elements.

An alternative is the use of Fourier Transform Infrared Spectroscopy (FTIR), which is both rapid, non-destructive and requires small, < 1 mg, sized samples. Chemical bonds vibrate at a characteristic frequency representative of their structure, bond angle and length. Accordingly, individual molecules have the ability to interact with incident radiation by absorbing the radiation at specific wavelengths. FTIR spectroscopy takes advantage of this by recording the energy absorption of a sample over a range of frequencies. Individual absorption peaks can then be identified and assigned to individual chemical bonds to qualitatively or quantitatively identify individual compounds in complex systems. Although solid state characterisation of silica and silicates obtained from biology, minerals and synthetic materials has been performed using XRF and FTIR in conjunction with one another, a direct comparison of the results pointing out the key features of each technique together with their advantages and limitations has not been reported (Temuujin et al., 2001; Nayak and Singh, 2007; Liu et al., 2007; Dwivedi et al., 2010).

Applications of FTIR have been widely used to assess the chemical structure of biogenic silica (see summary in Leng et al. (2009)) as well as issues of silica maturation, increasing the proportion of Q_4 to Q_3 bonds (Schmidt et al., 2001; Moschen et al.,

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2006) and dissolution in diatoms (Rickert et al., 2002; Loucaides et al., 2010). Whilst FTIR data has also been integrated via transfer functions to measure nitrogen, biogenic silica as well as organic and inorganic carbon concentrations in sedimentary records (Vogel et al., 2008; Rosén et al., 2010), this approach requires a training-set to be developed containing samples ranging in purity from 0–100%. With the contamination matrix in cleaned biogenic silica samples likely to vary between individual sites and with the need to develop a stand-alone technique suitable for analysing small samples that can not be first assessed by other geochemical methods in order to develop a training set, an alternative approach is required. Here we develop a rapid stand-alone FTIR mass-balancing calibration method for measuring contamination in biogenic silica samples and assess its potential in a sedimentary diatom record from Lake Baikal, Russia. With all samples previously analysed for contamination using XRF, employed here as an absolute measure of sample contamination (Mackay et al., 2010b), a direct comparison of the two techniques can be undertaken and the advantages/disadvantages of the proposed FTIR method assessed. This novel approach provides the first direct quantitative comparison of silica and silicates studies using XRF and FTIR with applications in geo/biochemical and palaeoenvironmental studies of minerals and biominerals.

2 Methods

2.1 Samples

For the purpose of this study two purified diatom samples are used as diatom end-members, assumed to be representative of clean fossilised diatom material. The first, BFC_{mod}, is the NERC Isotope Geosciences Laboratory (NIGL) within-laboratory diatom standard originating from a lacustrine diatomite deposit from California. The second is the marine diatom standard PS1772-8 from the South Atlantic Ridge. Diatoms in both samples are well preserved and show no signs of diagenesis or frustule dissolution (Chapligin et al., 2010). Whilst trace levels of contamination have been de-

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tected through XRF and light microscopy in BFC_{mod}, no impurities have been found in PS1772-8 (Chapligin et al., 2010).

Analysed samples ($n = 78$) are lacustrine diatoms from Lake Baikal, Russia, ranging in age from 112.4 ka BP to 133.0 ka BP (Marine Isotope Stages [MIS] 5e-6). All have been analysed for oxygen isotopes $\delta^{18}O_{diatom}$ following the application of conventional cleaning techniques to remove non-diatom material with sample purity assessed via XRF with aluminium used as a tracer of contamination (Mackay et al., 2010b). A contaminant end-member, assumed to be representative of that present in the "cleaned" Lake Baikal diatom material, subsequently referred to as "Silt", was obtained for three samples by dissolving the diatoms in NaOH and retaining the residue.

2.2 FTIR analysis

Previous analyses of diatom/biogenic silica samples with FTIR have involved the creation of a KBr pressed pellet (Fröhlich, 1989). To avoid losing material this approach was not followed. Instead samples were analysed using single-bounce Attenuated Total Reflection FTIR (ATR-FTIR) where raw material is placed directly onto the diamond crystal for data acquisition. Samples data were recorded using a PerkinElmer Spectrum 100 and collecting eight scan from 380–4000 cm^{-1} with a resolution of 2 cm^{-1}. The data was post-analytical processed using fityk version 0.8.8 (Marcin, 2009).

FTIR spectra of pure silica typically exhibits peaks in two distinct regions (Fidalgo and Ilharco, 2001; Patwardhan et al., 2006): peaks at $> 2500\,cm^{-1}$ and $< 1300\,cm^{-1}$. The first region corresponds to hydroxyl (-OH) stretching from absorbed or molecular water, while the second region occurs due to several silica modes. Whilst containing a number of peaks, the silica region can be primarily separated into three peaks centred at: $\sim 450\,cm^{-1}$, $\sim 800\,cm^{-1}$ and a broad peak at $\sim 1100\,cm^{-1}$ (Fig. 1; Table 1). The absorption at $\sim 450\,cm^{-1}$ has been assigned to rocking motion of oxygen atoms bridging silicon atoms in siloxane bonds (Si-O-Si). The symmetric vibrations of silicon atoms in a silixane bond occur at $\sim 800\,cm^{-1}$ and are termed as υ_{as}-Si-O-Si. The largest peak observed in a silica spectrum is present at $\sim 1100\,cm^{-1}$ and is dominated

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by antisymmetric motion of silicon atoms in siloxane bonds (υ_{as}-Si-O-Si). This broad peak consists of three components: (i) a broad shoulder centred at 1115–1130 cm^{-1} assigned to longitudinal optical mode (LO υ_{as}-Si-O-Si); (ii) a strong peak centred at 1035–1045 cm^{-1} (transverse optical mode TO υ_{as}-Si-O-Si); and (iii) a weak absorption at 950 cm^{-1} due to silanol (Si-OH) stretching vibrations.

With other wavenumbers dominated by a high noise to signal ratio, this manuscript focuses on the silica region between 700–1300 cm^{-1} where the main spectral peaks for both end-members were observed. Following baseline correcting all spectra to zero, wavenumbers outside the range of 700–1300 cm^{-1} were therefore removed from the dataset to increase the signal:noise ratio. After normalisation of the spectra to enable the comparison of individual samples, peak deconvolution using gaussian peak fitting was performed on the diatom and "Silt" end-members with the resultant fitted models (Fig. 1), mBSi and mSilt respectively, extracted for use in the calibration models (Sect. 2.3). For the Baikal "Silt" samples, spectra were mean averaged prior to peak fitting to produce a single contaminant end-member model.

2.3 FTIR mass-balancing

By assuming that the spectrum of any Lake Baikal sample reflects the weighted relative abundance of the diatom and "Silt" end-member spectra, a mass-balanced matrix (**T**) can be created for each diatom/"Silt" end-member combination to define the spectrum expected for a given fraction of contamination, *c*, and diatoms (1-*c*) in a sample at wavenumber *w* (Fig. 2):

$$\mathbf{T} = [(1-c)\mathrm{mBSi}(w) + (c)\mathrm{mSilt}(w)]_{w=700,700.5,701,\ldots,1300:c=0,0.0001,0.0002,\ldots,1} \quad (1)$$

Following construction of **T**, measured FTIR spectra for each Lake Baikal sample are fitted against each modelled spectrum, **T**[*,*c*], with the Euclidean distance between the measured and modelled spectra, $\mathrm{Residual}_c$, used to calculate the goodness of fit and so the proportion of the measured spectra not accounted for by the modelled spectra,

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for a given level of contamination:

$$\text{Residual}_c = \sqrt{\sum_{w=700}^{1300} (\text{Sample}_w - \mathbf{T}[w, c])^2} \quad (2)$$

where Sample_w is spectra of the sample at wavenumber w. The optimum best fit model for each sample, and so amount of contamination, is identified by the fitted model with the lowest value of Residual_c (Fig. 3).

3 Results

3.1 Reproducibility

FTIR analyses of different aliquots of a single sample typically produce identical spectra. In some instances, usually in samples containing higher amounts of contamination, variable spectra are observed. Following model fitting the mean analytical reproducibility (1σ) from these aliquots in terms of contamination is <1% for samples containing less than 10% XRF contamination, 6% for samples containing 10–15% XRF contamination and 12% for more heavily contaminated samples. Combined with the small sample sizes required for FTIR analysis, < 1 mg, this variability is attributed to poor homogenisation in contaminated samples. To avoid homogenising by grinding, which may cause problems in subsequent sample preparation stages as well as geochemical and isotopic analyses and taxonomic identification, up to three aliquots were analysed per sample with the mean spectra used in subsequent calculations. The good reproducibility for samples containing only small amounts of contamination is more than sufficient for FTIR to be used in obtaining accurate estimates of sample contamination. Conversely, evidence of large variability in a sample FTIR spectra would be qualitative evidence of significant levels of impurities in the analysed sample.

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3.2 FTIR spectra

FTIR analysis of the three contaminant samples that make up the "Silt" end-member produce near identical spectra, validating the approach here of combining the three samples to create a single "Silt" contaminant end-member. Significant variability between these samples would have suggested the existence of different contamination matrices between individual samples, requiring the creation of FTIR models including two or more contaminant end-members (see Section 4). Comparisons of the FTIR spectra for the diatom standards BFC_{mod} and PS1772-8 against the Baikal "Silt" illustrates the significant differences between the end-members (Fig. 2). Accordingly, qualitative analysis of the Lake Baikal FTIR sample spectra against these end-members before calculation of T and Residualc provides a means of identifying samples that are significantly distorted away from the BFC_{mod}/PS1772-8 spectra and so heavily contaminated by non-diatom components (Fig. 4).

3.3 Model fitting

Application of the FTIR models to the Lake Baikal samples produces results that are broadly similar to those achieved using XRF, although significant over and under estimation is apparent for some samples (Fig. 5a, b). Although XRF analyses indicate small levels of contamination in BFC (Al_2O_3 = 2.0 wt.%) compared to PS1772-8 (Al_2O_3 = 0.09 wt.%) (Chapligin et al., 2010), using the PS1772-8 end-member only marginally reduces the difference between XRF and FTIR estimates of contamination. However, residual values from the fitting of the FTIR models against PS1772-8 are significantly lower at c. 5% for most samples, suggesting that the PS1772-8 end-member produces more accurate results with better identification of the optimal FTIR model (Fig. 5c). In an attempt to further reduce residual sizes, a three end-member training set was constructed consisting of BFC or PS1772-8 and standards of mica and montmorillonite to reflect the composition of the clay mineralogy in the Lake Baikal sediment record (Fagel and Mackay, 2008) (Fig. 6). Whilst residual are marginally lower under

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these three end-member models compared to the original two end-member models, comparison of Residual$_c$ suggest an overall deterioration in the accuracy of the contamination data when comparing the FTIR and XRF techniques (Fig. 7).

4 Discussion

Ideally contaminant end-members should be based on residue material that has been removed in the later stages of sample preparation, and so treated in the same manner as far as possible as contaminants in the analysed biogenic silica samples. Although this approach is used here with the same FTIR spectra observed for the three samples that comprise the "Silt" end-member, residual values of 2.8%–19.4% for both the two and three end-member FTIR models suggest that "Silt" is not fully representative of all the sample contaminants (Figs. 5c, 7c). Improved consideration is therefore required into how the contamination matrices can vary between samples from the same site to improve the accuracy of the model fitting and so estimates of contamination.

In spite of this, results suggest that this novel FTIR mass balancing method remains a valuable tool in assessing sample contamination/purity. Firstly, visual qualitative analysis of the FTIR sample spectra permits a simple means of identifying samples that are significantly different to the diatom end-member spectra prior to fitting to the training set data (Fig. 4). Confirmed by XRF estimates of sample contamination, this provides a rapid means of assessing purity prior to further isotope/geochemical analysis and allows the identification of samples that require additional cleaning without losing material to destructive techniques such as XRF. Secondly, quantitative changes in FTIR contamination closely follow the main changes in XRF contamination (Fig. 5a). Whilst large offsets are apparent between the XRF and FTIR data for some samples, these difference in contamination are on average 5.6% across the whole data-set and 4–5% for samples containing less than 20% XRF contamination. Repeating the FTIR model calculations using a diatom end-member created from the five cleanest Lake Baikal diatom samples, based on XRF measurements which indicate no contamination in these

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samples, reduces the offsets between XRF and FTIR to 3.1% across the whole dataset and 2.2% for samples containing less than 5% XRF contamination (Fig. 5: Baikal "Silt" training set). This, combined with marginally lower values of Residualc, may suggest that more accurate results can be be achieved by developing specific diatom/biogenic silica end-member for each site. Whilst the offset/error between the FTIR and XRF methods continues to rise with XRF contamination, the FTIR technique nonetheless is able to identify the samples as being contaminated, fulfilling the requirement for the method to determine whether a sample is clean for analysis.

An unusual feature of the dataset are recurrent peaks ($n = 6$) when XRF estimates of contamination are low and FTIR estimates are high at 20-40% (Fig. 5a, b, arrows). All are further marked by a significant increase in both Residualc and in the variability of replicate sample FTIR analyses (Fig. 5c). Analysis of these samples under a light microscope reveals moderate amounts of organic matter contamination and micron to sub-micron particles adhering to the frustules. The erroneous FTIR results and high residuals can therefore be attributed to the absence of an appropriate organic matter end-member in the FTIR calibration. Whilst visual analyses suggest these samples are not 20–40% contamination, as indicated by FTIR, some level of contamination is undoubtedly present at levels beyond those documented by XRF when using aluminium as a tracer of contamination. Whilst the percentage Loss On Ignition (LOI) obtained during XRF bead fusion at ca. 1050 °C provides some information on organic matter and carbonate concentrations, isolating this information from occluded water and other weight losses related to diatom silica exchanges is problematic. Consequently, XRF should not be regarded as a perfect means of assessing sample contamination when organic matter and other volatile compounds are present. Instead a combined XRF and FTIR approach may be optimal for fully identifying samples that contain unacceptable levels of contamination.

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4.1 Implications for palaeoclimatic research

Diatom and biogenic silica derived isotope and geochemical records are increasingly being identified as important tools in generating climatic and environmental reconstructions at sites where carbonate are not readily preserved in the sediment record. Existing research for example, encompassing both high and low latitude regions, has been marked by investigations using diatom δ^{15}N and δ^{30}Si to study the role of the Southern Ocean biological pump and silicic acid leakage in regulating atmospheric CO_2 over glacial-interglacial cycles (Beucher et al., 2007). Similarly, use of diatom δ^{18}O has led to the detection of hydrological changes in both Africa and Scandinavia (Barker et al., 2007; Jonsson et al., 2010) whilst diatom Zn/Si ratios are beginning to be developed as proxies in both marine and non-marine settings (Hendry and Rickaby, 2008; Jaccard et al., 2009).

Although the vast majority of these records are valid, in some instances it has been demonstrated that analysed sequences have been contaminated by non-diatom material (Brewer et al., 2008). This can severely inhibit attempts to generate the accurate records required for quantitative reconstructions and, more seriously, lead to erroneous climatic interpretations being made. For example in a deglacial Holocene record from Lake Baikal a 5–10‰ decrease in δ^{18}O, indicating significant changes in lake hydrology and regional Siberian climatology, was subsequently found to almost entirely originate from the presence of micron to sub-micron clay contaminants adhering to diatom frustules (Morley et al., 2005; Brewer et al., 2008). With even small amounts of contamination capable of varying both geochemical and isotope measurements outside of analytical error, it is necessarily to accurately eliminate such errors and verify the reliability of published data. The demonstration here of a simple quantitative method for identifying "unclean" samples, contaminated by both organic and non-organic compounds, provides a solution to this and prevents resources being wasted by analysed contaminated samples.

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5 Conclusions

A simple rapid and non-destructive FTIR technique is presented here detailing a geochemical approach for assessing biogenic silica purity in small, < 1 mg, sized samples. With results from this method in line with those from XRF analyses, the technique is appropriate in instances requiring quick and routine assessments of sample purity, e.g., during sample preparation, and where insufficient materiel exists for other geochemical analyses (e.g., Lake Baikal samples #1–8 where insufficient material exists for XRF analysis). Such an approach would significantly reduce the time lost by analysing unclean samples for isotope/other geochemical techniques. Issues of sample homogenisation can be resolved in contaminated samples by repeated FTIR analyses of different sub-aliquots of a sample. Further work is needed to apply and test the FTIR method in other sites/samples containing both diatoms and other forms of biogenic silica in order to better understand the methods potential in measuring levels of contamination. In particular, moderate to high residual errors in some samples from the fitting of the FTIR spectra suggests that improvements could be obtained through the development and use of more refined end-members for each set of samples. In the interim, by assessing levels of contamination using both FTIR and XRF, the potential limitations associated with each technique can be overcome to provide a better insight of contamination levels. Such steps are essential if mistakes in analysing and interpreting contaminated sequences are to be avoided and biogenic silica isotope/geochemical records are to be used to their full potential in generating reliable palaeoenvironmental reconstructions.

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Table 1. Peak information for the BFC_{mod} FTIR spectra in Fig. 1.

Peak Centre cm^{-1}	Area (% of BFC_{mod} FTIR spectra)
751.78	0.35
785.49	1.28
806.18	4.21
939.82	6.32
965.97	0.64
1031.96	6.16
1066.18	62.02
1100.26	0.91
1172.48	15.19
1231.31	3.09

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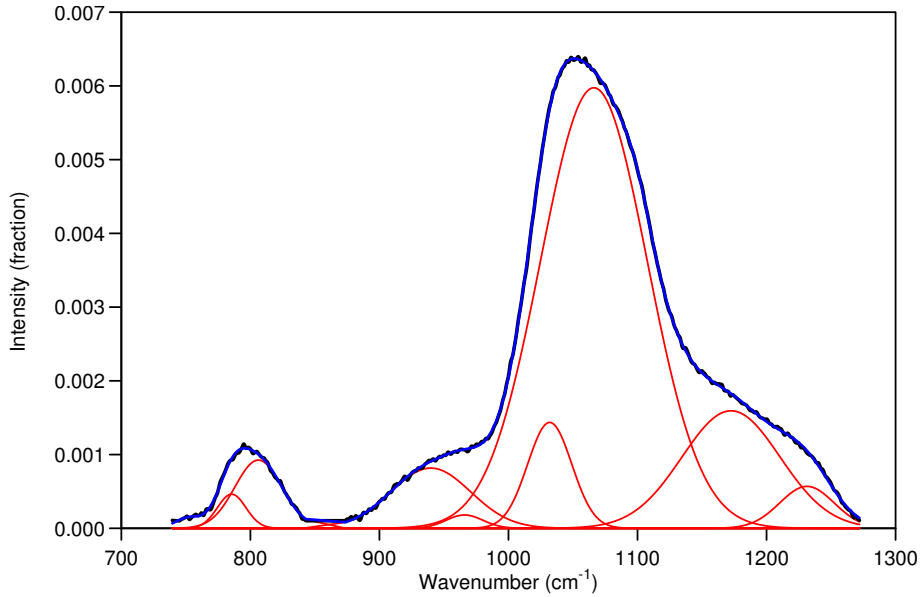

Fig. 1. Example of gaussian peak fitting (red curves) for the BFC_{mod} FTIR spectra (Table 1). The resultant fitted model is subsequently used to develop the BFC_{mod}–"Silt" mass-balance calibration.

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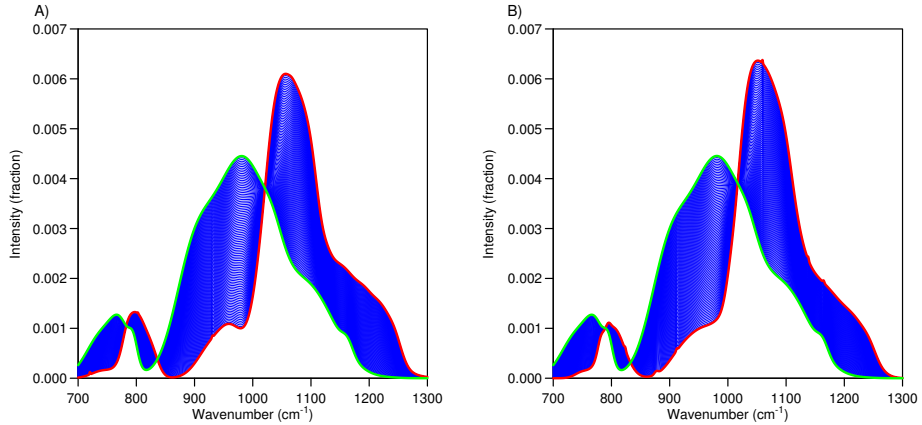

Fig. 2. Mass-balance models for the BFC_{mod}–"Silt" **(A)** and PS1772-8–"Silt" **(B)** end-members. Red and green lines show the baseline corrected FTIR spectra for the pure diatom and "Silt" end-members respectively. Blue lines show the expected modelled spectra for samples containing different proportions of diatoms/contaminants. Samples containing 100% diatoms/contaminants are expected to plot on the diatom/"Silt" end-member spectra respectively. As the proportion of diatoms in the sample decreases, sample FTIR spectra are expected to progressively plot away from the red, pure diatom, spectra towards the green, pure "Silt", spectra.

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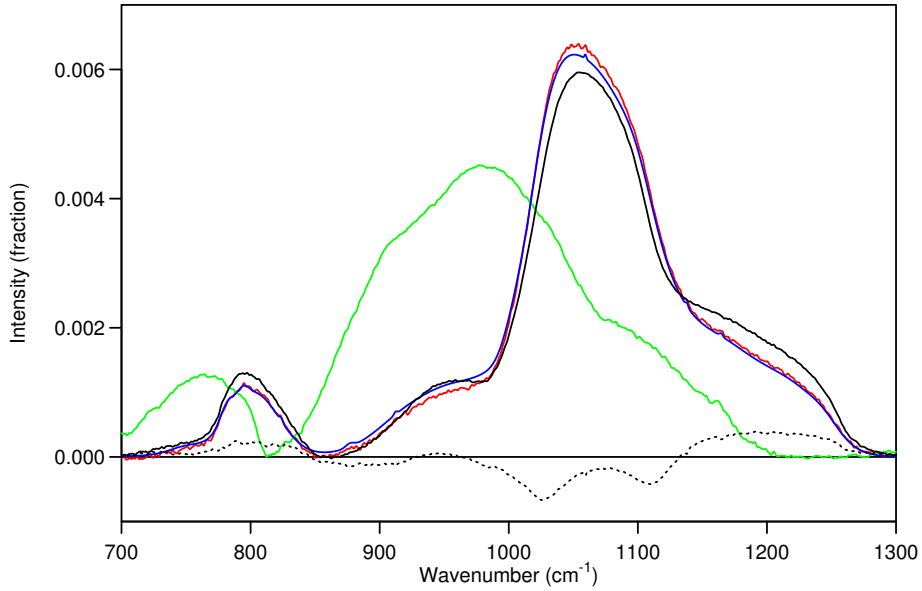

Fig. 3. Example of a Baikal diatom sample (#36) fitted against the BFC_{mod}–"Silt" mass-balance matrix. Red line = BFC_{mod} spectra, Green line = "Silt" spectra, Black line = Baikal sample #36 spectra; Blue line = optimum, best fit, modelled spectra for sample #36 in the BFC_{mod}–"Silt" matrix; Dashed line = residual spectra from the fitting of the #36 spectra against the modelled spectra. For #36 XRF contamination = 6.1%, FTIR contamination = 3.8%.

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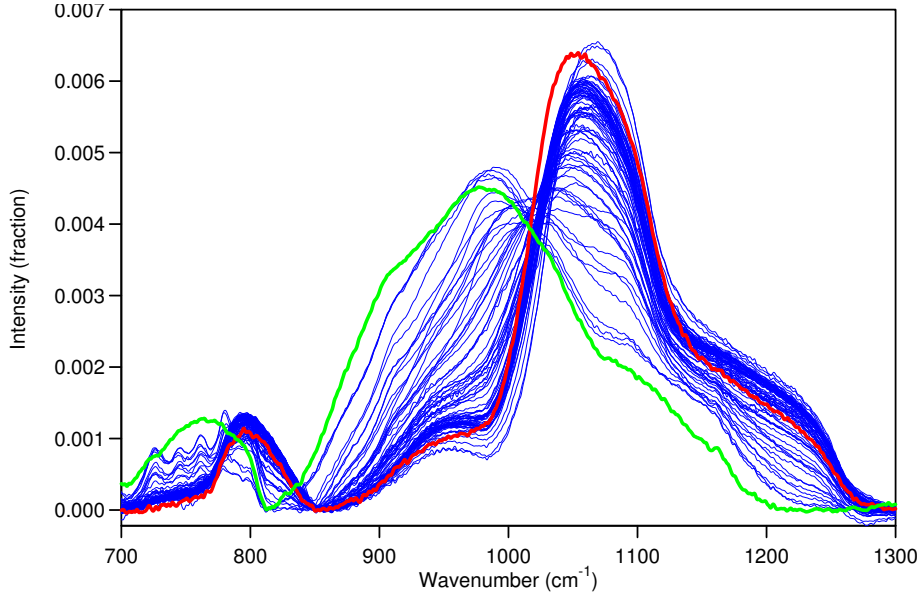

Fig. 4. Comparisons of the Lake Baikal FTIR sample spectra (blue lines) against the BFC_{mod} (red line) and "Silt" (green line) spectra. Spectra of contaminated samples are either aligned to the "Silt" spectra or to a mixture of the diatom/"Silt" spectra.

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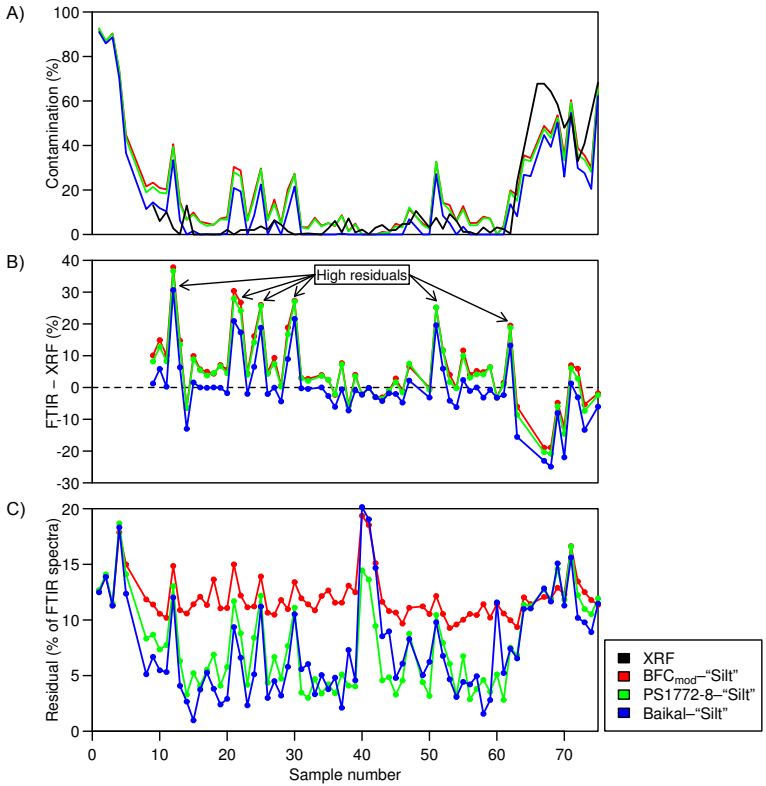

Fig. 5. FTIR two end-member results: **(A)** FTIR and XRF estimates of contamination in Lake Baikal samples; **(B)** FTIR minus XRF estimates of contamination. Positive/negative values indicate FTIR over/under-estimation of sample contamination; **(C)** Residuals from the fitting of the sample FTIR spectra against the best-fit modelled FTIR spectra. No XRF results for some samples indicates the absence of sufficient material for XRF analysis.

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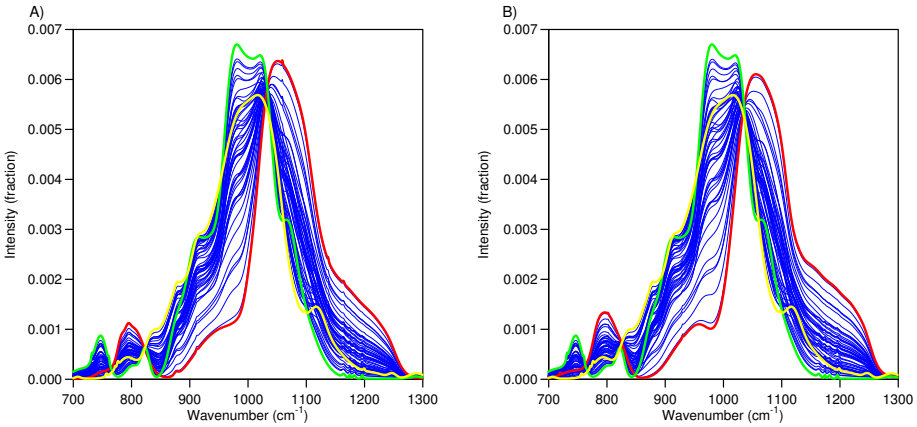

Fig. 6. Mass-balance models for the three end-member models including FTIR spectra for diatoms (red line), mica (green line) and montmorillonite (yellow line) for: **(A)** BFC_{mod}; **(B)** PS1772-8. Blue lines show the expected spectra for samples containing different proportions of diatoms/contaminants. As the proportion of diatoms decreases, spectra are expected to progressively plot away from the pure diatom spectra and towards the mica/montmorillonite spectra. For clarity only a random 50 out of the 5151 (at 1% resolution) possible end-member spectra combinations are shown.

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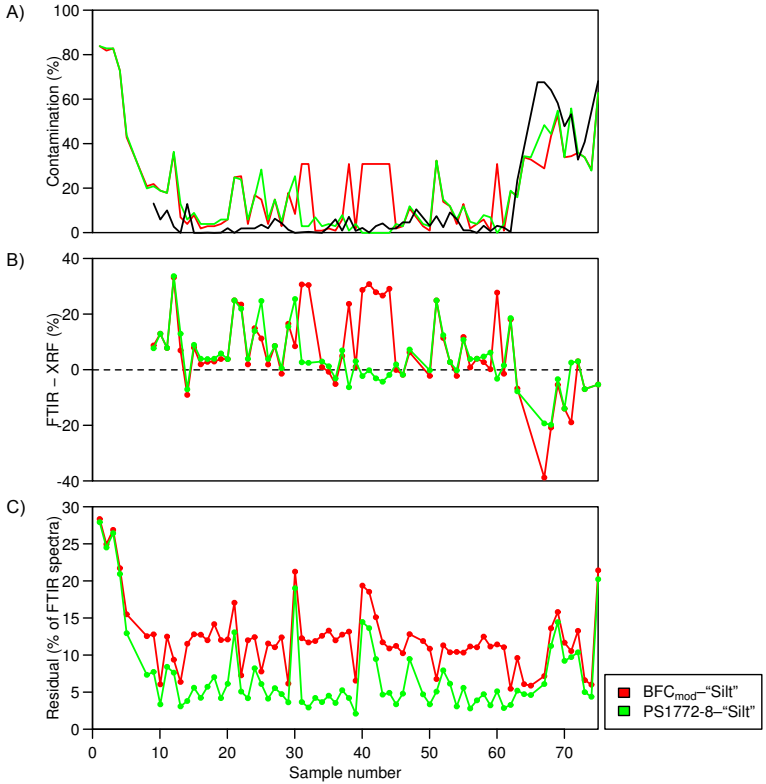

Fig. 7. FTIR three end-member (diatom, mica and montmorillonite) results: **(A)** FTIR and XRF estimates of contamination in Lake Baikal samples; **(B)** FTIR minus XRF estimates of contamination. Positive/negative values indicate FTIR over/under-estimation of sample contamination; **(C)** Residuals from the fitting of the sample FTIR spectra against the best-fit modelled FTIR spectra. No XRF results for some samples indicates the absence of sufficient material for XRF analysis.

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